

Environmental Transport and Transformation of Automotive-Emitted Lead

by Warren T. Piver*

The use of a mass balance equation assists in clarifying the contribution of automotive-emitted lead to the regional and global problems of the distribution of this element, by taking into account the physicochemical transformation processes operating on the lead during its transport along the various environmental pathways. The technical factors which govern the emission of such lead from automobile engines and which affect its subsequent dispersion through the environment are described.

Introduction

This paper deals with the fate of particulate lead compounds emitted to the atmosphere from the combustion of leaded gasoline in spark-ignition engines. It is concerned with not only how these emissions are initially partitioned between air, water, and solid phases when discharged from the tailpipe, but also the way in which the partitioning varies with time due to the physicochemical properties of these emissions and to the environmental transport and transformation processes which act upon them.

Because there are many properties and processes which influence the fate of lead particles in exhaust emissions, use will be made of a mass balance as a simple method of keeping track of the properties and processes which influence the partitioning of particulate lead emissions. For a given geographical area, this mass balance can be written as shown in Eq. (1):

$$\left[\begin{array}{l} \text{Rate of lead particulate} \\ \text{emission into atmosphere} \\ \text{by motor vehicles moving} \\ \text{through geographical area} \end{array} \right] - \left[\begin{array}{l} \text{Rate of lead removal} \\ \text{from geographical} \\ \text{area by physical and} \\ \text{chemical processes} \end{array} \right] = \left[\begin{array}{l} \text{Rate of accumulation} \\ \text{of lead within} \\ \text{geographic area} \end{array} \right] \quad (1)$$

*Office of Health Hazard Assessment, National Institute of Environmental Health Sciences, Research Triangle Park, North Carolina 27709.

The use of the conceptual framework of a mass balance for cataloging the properties and processes which influence the partitioning of lead exhaust emissions is similar to that used by Huntzicker et al. (1) in their material balance study of automotive-emitted lead in the Los Angeles Basin. With this method, the predominant rate processes can be identified, and an actual solution of the final expression is possible with certain restrictions. In addition, the mass balance concept yields a useful method of analyzing the immediate effects of lead exhaust emissions and their probable future impact and provides data for planning future methods of control.

The terms in this mass balance have units of mass flux (lb/day-square mile). It provides a sensitive indicator of the impact of a pollutant on a particular geographical region. In terms of public health impact, the geographical regions of most concern in the United States are the Standard Metropolitan Statistical Areas (SMSAs) in which 155 million (73.2%) of the population live (2). These SMSAs comprise about 0.388 million square miles or 10.7% of the total United States land area of 3.615 million square miles (2). Thus there is a population density of approximately 400 people per square mile in metropolitan areas compared with an average density for the entire United States of approximately 59 people per square mile, and of approximately 17 people per square mile for rural areas. The mass flux of lead exhaust emissions entering an urban

region can be estimated from the emission rate in pounds per vehicle mile driven, the total number of vehicle miles driven per day, and the land area of the urban region. This emission rate is a function of the sales volume of different leaded gasoline grades, driving patterns, and characteristics of the engine-exhaust system.

The first term in Eq. (1) representing the mass flux of lead into a geographic region implies that lead enters principally as an exhaust emission from motor vehicles. Within any given geographical region, lead can be introduced or mobilized by a number of technological and natural activities. Examples of the former include the operation of lead smelters and lead storage battery plants, the combustion of fossil fuels for power generation and space heating, and the incineration of municipal and industrial wastes and sewage sludges. Natural processes include mobilization of lead from bottom sediments into streams, evaporation of lead gasoline from storage tanks at filling stations and in motor vehicles, flaking of lead-based paint from old buildings, fallout from the atmosphere via sedimentation and precipitation of lead particles transported to this region from distant areas, and transport through the region by flowing bodies of water. Not all of these processes contribute significant amounts of lead to the environment within any given geographical region, but they are all listed for the sake of completeness.

The second term in the mass balance is the mass flux removal term. Processes which are appropriate for this category are dispersion and chemical transformation in the atmosphere, runoff from soil, roadways, and streets into streams, rivers, and oceans caused by precipitation and streetwashing, reentrainment of particles and transport by atmospheric processes, and the movement in commerce of foods containing lead.

The third term in the mass balance describes the rate of accumulation of lead within a region after the rate of removal has been subtracted from the rate of entry of lead. The inclusion of this term results in an unsteady-state mass balance which now requires that the meaning of lead accumulation within a region be defined.

Before describing each term in the mass balance in more detail, it is necessary to explain why lead exhaust emissions from motor vehicles have been designated as the primary source of lead entering a given geographic region. The geographic regions of most concern are the metropolitan areas.

In 1968, on a national basis, the greatest contributor of lead to the environment from anthropogenic activities was the combustion of leaded gasoline (3). Of an estimated total of 184,316 tons

emitted, 181,000 tons/yr were from the combustion of leaded fuel. Of the remaining 3,316 tons, 910 tons/yr were contributed by coal combustion; 811 tons/yr were contributed by secondary lead smelting; 810 tons/yr came from lead alkyl manufacture; 521 tons/yr were from brass manufacture; 174 tons/yr from primary lead smelting; 36 tons/yr from gasoline transfer; 24 tons/yr from fuel oil combustion; and 20 tons/yr from lead oxide manufacture (3). In 1968, United States sales of lead fuel additives amounted to 241,067 tons (4). Assuming that this total was consumed primarily in the United States, approximately 75% of the lead in gasoline consumed in spark-ignited engines was emitted as exhaust emissions to the atmosphere. The fate of the remaining 25% will be considered in a later paragraph.

Another source of environmental lead, particularly in urban regions, is the flaking and peeling of leaded paint from interior and exterior painted surfaces. The principle constituent of lead-based paint is white lead. The name "white lead" is applied primarily to basic lead carbonate but also refers to basic lead sulfate and basic lead silicate. The consumption of white lead has been declining steadily from 80,000 tons in 1935, to 36,000 tons in 1950, to 6,000 tons in 1968 (5). Over the same period, lead fuel additive consumption rose from 37,000 tons in 1935, to 114,000 tons in 1950, to 241,000 in 1968 (5). The high levels of lead found in soil adjacent to buildings painted with lead-based paints has been attributed principally to the peeling and flaking of these surface coatings, but estimates of rates of peeling are not available. In addition, insufficient attention has been given to the amount of lead in soil near buildings which was contributed by the washoff of lead-containing dust and dirt deposited on building surfaces by sedimentation and impaction of lead in exhaust emissions. Even so, from 1950, compared to the rate of entry of lead from exhaust emissions, the entry of lead via flaking paint, based on its production and use, is considered negligible.

In 1965, Patterson (6) estimated that the amount of lead mined and introduced into urban areas each year was more than 100 times the amount leached from soils and added to streams and the world's oceans. In 1965 mine production of lead was about 450,000 tons and in 1968 mine production of lead was about 500,000 tons (5). The principal natural method by which lead enters the surface environment is by leaching from soils. Estimates of the amount mobilized in this way have not been supported by experimental evidence, but even if they were out by an order of magnitude, they would still be negligible in comparison to the amounts added

from the combustion of leaded fuel in motor vehicles.

Since 1970, sales of lead fuel additives in the United States have declined from 242,182 tons in 1970 to 150,075 tons in 1975—an overall drop of 38% in five years (7, 8). This decline in the sales of leaded fuel is attributed to the introduction starting in the late 60's of lower compression engines with lower octane fuel requirements. With the introduction of oxidation catalyst-equipped vehicles in 1975 to meet exhaust emission standards for carbon monoxide and hydrocarbons, the market for leaded fuel should continue to decline. Even so, exhaust emissions from the use of leaded gasoline in pre-1975 vehicles will remain a major source of lead release to the environment for some time, and, because of the greater population and number of motor vehicles in urban areas, these are the areas which will receive the greatest mass flux of lead from exhaust emissions.

Rate of Lead Particulate Emission from Motor Vehicles

The factors which affect both the rate of particulate lead emissions and the physicochemical properties of these emissions are: the lead content of the fuel, the driving speed or mode of driving, and the design and operational features, maintenance, and age of both the engine and the exhaust system. The important physicochemical properties of the particulate emissions are: the total amount emitted, the size distribution of the particles, and chemical composition of the particles as a function of particle size. The most commonly used index of particle size which is reported in experimental studies is the mass median equivalent diameter (MMED). This property is defined as the size distribution of particles such that half the mass lies on either side of the MMED (9). It is therefore average particle size determined on the basis of total mass. The equivalent diameter of a particle describes more than the geometric measurements of particle diameter. Since particle shape and density are taken into account, the definition makes it possible to describe the behavior in the atmosphere of a particle of equivalent diameter D (regardless of shape or density) by a sphere of unit density and diameter D .

Lead Content of Gasolines

The average contents of leaded gasolines sold at gas stations on a national basis have been determined by Jungers et al. (10). These average contents are: 600 $\mu\text{g/ml}$ (2.3 g Pb/gal) for premium grades; 494 $\mu\text{g/ml}$ (1.86 g Pb/gal) for regular grades;

and 134 $\mu\text{g/ml}$ (0.5 g Pb/gal) for low-lead grades. Lead fuel additives are a mixture of tetraethyl- and tetramethyllead. In many of the experimental studies on characterization of lead particulate emissions two special types of test fuel are used: Indolene HO O which contains no lead, and Indolene HO 30 which contains 3 ml tetraethyllead (TEL)/gal.

Driving Speed or Mode of Driving

A summary of data on how both constant driving speed and the seven-mode Federal Test Cycle (11–13) affect the physicochemical characteristics of lead particulate emissions has been compiled by Springer (14) and is shown in Table 1. Since this review, several additional studies on the characterization of lead particulate emissions have been reported by Moran et al. (15), Habibi (16), Ter Haar (17), and Boyer and Laitinen (18).

Measurements of particulate emissions have been made, both with engines mounted on dynamometers and with engines driven on chassis dynamometers. Experiments have been performed for constant vehicle speeds, accelerating engines, decelerating engines, and for engines operating under definite driving cycles. As the cruise speed increases, both the rate of emissions and the MMED of the particulate emissions increases. Data from Ter Haar et al. (19) show that the fine lead particles (MMED less than 0.5 μm) emitted at a constant cruise speed of 25 mph contribute approximately 92% of the particulate exhaust emissions, while at a constant cruise speed of 60 mph, fine lead particles constitute only 69%. In addition the total exhaust emission rate increases with increasing speed. It has been demonstrated that at constant speed or cruise conditions, lower emission rates are observed than when an engine is accelerating. During acceleration, the emission rate and the MMED of the particles increases because the rapid change in speed tends to dislodge deposits which have built up along the length of the exhaust system. In measurements of full-throttle acceleration tests, Hirschler et al. (20, 21) recorded emission rates 200% greater than the fuel lead input rate. Emission rates for an initially cold engine are much higher than for an engine which has been stopped after it was warmed up and then restarted again (hot start versus cold start). In addition, Ninomiya et al. (22) demonstrated that several test cycles were necessary before the emission rate dropped to a stable level.

Because particulate emissions are not regulated emissions, no standard test procedure has been written for characterizing particulate exhaust emis-

sions. However, the seven-mode Test Cycle and the Federal Mileage Accumulation Schedule (12) which were developed to measure exhaust emission rates for the regulated exhaust emissions of carbon monoxide, hydrocarbons, and nitrogen oxides, have been adapted for this purpose. Even so, individual drivers and individual engines will produce their own unique sets of results for emission rates and particulate characteristics.

Several additional points are noteworthy. During normal driving operations, Hirschler and co-workers (20, 21) observed that approximately $\frac{1}{3}$ of the total lead used in combustion remains in the vehicle. Part of the lead is deposited on the surfaces of the engine-exhaust system and part ends up in the lubricating oil due to leakage around the piston rings. Ter Haar et al. (19) presented data which indicate that approximately 25% of the lead in gasoline burned in the engine is not emitted in the vehicle's exhaust. It is estimated that 10% of the lead consumed during combustion is released to the environment via disposal of waste lubricating oil. To demonstrate how vehicle speed affects the percent of lead emitted in the exhaust, Ganley and Springer (23) plotted the ratio of lead emitted in the exhaust of the amount of lead taken into the engine as a function of vehicle speed. When plotted in this manner, the percentage of input lead emitted in the exhaust increased from approximately 15% at 25 mph (constant speed) to between 50 and 90% at 70 mph. These results are detailed in the following sections.

Leaded Fuels. Lead particulate emission rate increases as constant vehicle speed (cruise) increases. For both low and high constant vehicle speeds, lead particulate emissions are generally less than $0.5 \mu\text{m}$ MMED.

As the lead content of gasoline increases, the weight concentration of particles and the emission rate increases for all types of driving modes.

For the seven-mode Federal Test Cycle, lead emissions increase as fuel lead content increases. It should be remembered that this test procedure includes constant vehicle speed operation, acceleration, and deceleration types of driving. Therefore, the emission rate for the seven-mode Federal Test Cycle is an average rate for all of these different types of driving operations. It is well demonstrated that acceleration produces higher emission rates than cruise conditions but it would be difficult to compare these two types of driving on an absolute basis.

The major chemical form of lead in particulate emissions for all types of driving conditions is the mixed halide, PbBrCl . Other minor constituents are

PbCl_2 , PbClBr , $(\text{PbO})_2$, PbO , PbSO_4 , PbSO_3 , $\text{Pb}_3(\text{PO}_4)_2$, PbClBr , and $\text{PbClBr} \cdot \text{NH}_4\text{Cl}$. Fe_2O_3 is also a major constituent of large particulate emissions. In addition, unspecified carbon compounds are also part of these emissions.

The identification by Ter Haar and Bayard (24) of $(\text{PbO})_2\text{PbBr}$, PbSO_4 , and $\text{Pb}_3(\text{PO}_4)_2$, and $\text{Pb}(\text{OH})\text{Br}$ as constituents of particulate exhaust emissions has been challenged by Heidel and Desborough (25).

In experimental studies fine particles in exhaust emissions are nearly spherical in shape (26) and coarse particles have a much more irregular shape (23). Particles collected at a constant cruise speed of 30 mph were composed of a carbon core which held adsorbed to it polynuclear aromatic hydrocarbons of two to six-membered rings (18). In other studies, this core was overlaid with lead particles and double salts which had condensed from the vapor phase (23). In the environment, lead particles (collected near Fleet Street in London) showed no such regular geometry (26). Morphologically the fine lead particles were dispersed in a matrix of carbonaceous material.

Unleaded Fuels particulate emission rates are generally lower than for leaded fuels. For comparable driving conditions, chemically, the particles are mostly carbon with adsorbed multi-ring polycondensed aromatics which are formed during the combustion process. The particulate emission rate increases as the aromatic content of the fuel increases.

Effect of Design Features, Operating Conditions, and Age of Both the Engine and the Exhaust System

Variations in air/fuel ratio and spark timing have very little effect on the emission rate and the characteristics of particulate emissions (23, 27). Table 1, however, demonstrates how cold start versus hot start conditions and the number of driving cycles influence the rate of exhaust particulate emissions (22).

The design, operating conditions, and age of the engine-exhaust system have been shown to have an important influence on the characteristics of particulate lead emissions. The axial temperature along the length of the exhaust system is a function of the driving speed (28). Sampson and Springer (27) and Ganley and Springer (23) have demonstrated how axial temperature and exhaust gas temperature influence the emission rate and weight concentration of particulate emissions. For a cruise speed of 55 mph and Indolene HO 30 leaded fuel, there was a

Table 1. Physicochemical characteristics of particulate emissions for different engines, different fuel lead content, and different modes of driving.

Engine	Operating conditions	Fuel composition	Total emission rate, g/mile	MMED, μm	Chemical composition of particulate emissions	Reference
1954 Chevrolet, 6 cyl	30 mph cruise	Not specified	0.15	Not given	At 30 mph, avg. Pb content 50% wt.; Fe_2O_3 content 1 wt-%. At 50 mph, avg. Pb content 90 wt-%; Fe_2O_3 content 10 wt-% lead PbBrCl	McKee and McMahon (82)
1954 Oldsmobile V-8	50 mph cruise		0.15			
1954 Plymouth, 6 cyl	30 mph cruise		0.04			
	50 mph cruise		0.1			
1957 Oldsmobile, V-8	30 mph cruise		0.06			
	50 mph cruise		0.23			
1957 Chrysler, V-8	30 mph cruise		0.08			
	50 mph cruise		0.03			
1957 Ford, V-8	30 mph cruise		0.06			
	50 mph cruise		0.49			
Various 1966 models; average deposit mileage 51,000	30 mph cruise		0.1			
	50 mph cruise		0.14			
	7-mode Federal Test Cycle	Leaded fuel	Not given	Not given	Pb content of particulate emissions 17 wt-%; carbon content 34% wt-% lead as PbBrCl	Ter Haar et al. (19)
Various 1966 models; average deposit mileage 30,000-50,000 mi.	4 cold starts		0.51			
	4 hot starts		0.24			
New cars 0-1,000 mi.	7-mode Federal Test Cycle	Unleaded fuel	0.32	Carbon content of particulate emission 70 wt-%		
	4 cold starts		0.13			
	4 hot starts					
Various 1963-1968 models; average deposits 20,000-62,000 mi.	7-mode FTC	Indolene + 3 ml TEL/gal.	0.20	90% of Pb are fines, $<0.5 \mu\text{m}$ $\frac{1}{3}$ coarse ($<5 \mu\text{m}$), $\frac{2}{3}$ fines	Pb = 13 wt-% C = 47 wt-%	Not given
	4 cold		0.12			
	4 hot starts		0.22			
	4 cold starts		0.11			
Various 1963-1968 models; average deposits 20,000-62,000 mi.	4 hot starts	Leaded fuel	0.029	90% of Pb are fines, $<0.5 \mu\text{m}$ $\frac{1}{3}$ coarse ($<5 \mu\text{m}$), $\frac{2}{3}$ fines	Not given	
	25 mph cruise		0.046			
	45 mph cruise		0.083			
	60 mph cruise					
	7-mode FTC		0.056			
327 CID, V-8	Hot cycles	3 ml TEL/gal	0.121	1.1	Not specified	Habibi (29)
	cold cycles		0.079			
	Full (35% cold, 65% hot acceleration (0-70 + 30-70))					
	Simulated consumer driving cycle		0.4			
	At 7,500 mi.					
1969, 350 CID, V-8	At 16,500 mi.	Leaded fuel		3.1	For particles $> 200 \mu\text{m}$: 50 wt-% is PbBrCl, 10 wt-% is PbBrCl · 2PbO, 3 wt-% is PbSO ₄ or PbP ₂ O ₇ ; 33 wt-% is C For particles 2-10 μm , PbBrCl is major constituent for particles $< 2 \mu\text{m}$, 2 PbBrCl · NH ₄ Cl	Habibi (16)
	At 21,500 mi			4.7		
	Simulated consumer driving cycle,		0.4	1.1-2.1		
	At 5,000 mi.			3.6-3.8		
	At 16,000 mi.			4.7-5.7		
1969 Ford, V-8 310 CID	At 21,000 mi.			>15		
	At 28,000 mi.					
	7-mode FTC	Leaded fuel	0.51	$<< 0.1$	Particulate emission composed of Pb, Br, Fe, and Zn	Ninomiya (22)
	Cold start after 10 cycles		0.27			
	Steady, 2250 rpm (about 55 mph)		0.16			
	Indolene HO O + 3 ml TEL/gal		0.15			
	Indolene HO O + 3 ml TEL/gal + 1.0 theory EDB		0.10			
1970 Chevrolet, V-8	Indolene HO 30 (3 ml TEL/gal + motor mix scavenger	Indolene HO 150.03 (1.5 ml TEL/gal)	0.10	0.65	For leaded fuels, particulate emissions composed of Pb, Br, Cl, and organics	Moran et al. (15)
	Indolene HO 150.03 (1.5 ml TEL/gal)		1.5			
	Indolene HO O					

rapid increase in particulate weight for an exhaust gas temperature drop between 640 and 470°F. This weight increase was attributed to the condensation of lead salt vapors onto a carbon particle core. By x-ray diffraction this material was identified as a mixture of PbCl_2 and PbBrCl . The particulate weight remained constant between a temperature range of 470–250°F. Below 250°F, the weight increased again, presumably due to condensation from the exhaust gases of high molecular weight organic compounds which boil in this temperature range.

Earlier, Hirschler and his co-workers (20, 21), and more recently Habibi (16, 29), examined how the age of the engine-exhaust system affects both the rate and physicochemical characteristics of particulate emissions from the combustion of leaded fuels in spark-ignited engines. Habibi's results are for the seven mode Federal Test Cycle. They may be summarized as follows: Lead particulate emissions are deposited along the length of the exhaust system. In addition, burned lead can be found deposited on engine parts and retained in the oil. During high-speed or high-load driving conditions (such as acceleration), these deposits can be re-entrained by the high velocity exhaust gases. There is a general increase in lead emissions with mileage accumulation. The effect of accumulated mileage on emission rates and MMED of emitted particles is shown in Table 1 (16, 29). In essence, average particle size on a mass basis increases as the age of the exhaust system (mileage accumulation) increases. Chemically, the very large particles ($>200\ \mu\text{m}$) are 60–65% lead, 30–35% Fe_2O_3 , and 2–3% soot. Particles $<2\ \mu\text{m}$ are composed of the salt $2\text{PbBrCl} \cdot \text{NH}_4\text{Cl}$. These results are summarized in Table 1.

Rate of Lead Particulate Emissions

From the foregoing discussion of factors which influence the rate and character of lead particulate emissions, the following observations may be made. For the seven-mode Federal Test Cycle, which involves low-speed cruise, acceleration, deceleration, and idle driving conditions, the production and emission of particles with MMED's less than $0.5\ \mu\text{m}$ is favored (19). Chemically, these particles will be composed mainly of PbBrCl which is preferentially deposited on the outer surfaces of the particle. For high constant speed tests, the rate of particulate lead emissions will be greater than for lower speeds. For all driving speeds the majority of particles will be fine particles, and chemically the lead salt will be PbBrCl , which is preferentially deposited on the particle surface. The MMED of the

particles increases with age of the engine-exhaust system for the seven-mode driving cycles and the large size (coarse) particles contain a higher percentage of lead salts than do the smaller size (fine) material.

Rate of Removal of Lead Particulate Emissions

Turbulent Dispersion of Airborne Lead

Many investigators have reported airborne lead concentrations. In 1968, the average annual concentration of lead particles in urban air ranged from 1 to $3\ \mu\text{g Pb/m}^3$ (3). In nonurban areas near cities, the average air concentration has been measured at $0.21\ \mu\text{g Pb/m}^3$, and for rural areas $0.10\ \mu\text{g/m}^3$ (30). Colucci et al. (31) found an annual average airborne lead concentration of $8.9\ \mu\text{g Pb/m}^3$ near a busy New York City highway and a level of $11.3\ \mu\text{g Pb/m}^3$ near a busy Los Angeles highway.

There have been many attempts to describe by mathematical simulation the movement of pollutants in the environment. The majority of these models originate from two fundamental approaches to describing turbulent diffusion. In the Eulerian approach, concentration changes are described from a fixed coordinate system. In validating these models with experimental results, independent variables such as wind speed and direction, are easily measured from a fixed position. Eulerian models can take into account complex atmospheric reaction mechanisms, variations in source strength, and variations in topography. The incorporation of so many components into the model makes precise analytical results difficult to obtain, and it is necessary to resort to approximate methods of solution. In the Lagrangian approach, spatial and temporal changes in pollutant concentration are described relative to a fluid parcel. Validation of these models is difficult because the variables in the expressions cannot be measured experimentally but must be estimated by statistical methods. Even with these restrictions both methods have been used to describe turbulent diffusion. With appropriate assumptions, each can provide reasonable estimates of pollutant dispersion in the atmosphere.

There are many references to the subject of atmospheric turbulence and dispersion of pollutants by turbulent diffusion. In particular, the treatises of Pasquill (32), Monin and Yaglom (33), Gifford (34), Lumley and Panofsky (35), and Seinfeld (36) provide a more rigorous description of the mathematics of these two approaches. The so-called "K" theory models originate from the Eulerian approach, and the Gaussian plume models are derived from the

Lagrangian approach. In the next two paragraphs, examples are given of the application of these two approaches to describing dispersion of lead from exhaust emissions. These examples serve only as a representative sampling of the extensive literature on this subject and provide illustrations of validated models for predicting how lead exhaust emissions are partitioned in the environment.

At the University of Illinois (37–39) an Eulerian model has been formulated which is based on the solution of the equation of continuity governing dispersion of particulate emissions of arbitrary size distribution from a line source by advection, turbulent dispersion, and gravitational settling. This model has been used to predict airborne concentration and settling flux isopleths for lead from exhaust emissions for a 168 square mile region contiguous to Urbana-Champaign, Illinois (40). In terms of ambient air lead concentrations, it was concluded from experimental measurements of airborne lead, that the greatest contribution for this region came from sources upwind (41). The quantity of material which was removed from the air by gravitational settling was determined from the terminal settling velocity of the particle. This velocity was estimated from Stokes' Law or the Stokes-Cunningham equation, depending on the MMED of the particle.

At Colorado State University, Gaussian plume models have been formulated and applied to the dispersion of lead in the environment. Katen (42) and Cermak et al. (43, 44), using a Gaussian plume model described short-range diffusion of lead particulate emissions from an isolated divided highway and in the urban area of Fort Collins, Colorado. In the highway study, the input strength of lead from exhaust emissions was approximated as a line source, and the airborne lead concentrations at steady state, showed an exponential-type decay in magnitude as distance from the highway increased. Actual measurements of airborne lead showed that at a distance of 50 ft from the edge of the highway, the model was overestimating the airborne level by 33%. In the urban study, steady-state concentration profiles for city street canyons were described. From these studies it appears that the majority of lead settles from the atmosphere at short distances from a divided highway. In a city canyon, over 80% of the total lead exhaust emissions settle near the street by gravitational settling or are removed by impaction with the solid surfaces of the buildings near the street.

Colucci et al. (31) and Huntzicker et al. (1) have attempted to quantify the amount of airborne lead removed from its region of origin by atmospheric diffusion. Both groups have made a correlation between airborne lead and carbon monoxide. On the

basis of simultaneous measurements of lead and CO with corrections for other sources of these two pollutants Huntzicker et al. (1) have determined a ratio of lead to CO of $(6.2 \pm 1.6) \times 10^{-4}$. For the Los Angeles Basin, it was estimated that approximately 31% of the lead emitted by automobiles was removed by atmospheric diffusion of airborne lead particles and vapor phase organic lead compounds. The measurement of vapor phase organic lead compounds has been reported by Purdue et al. (45) and by Snyder (46). Since there are losses to the atmosphere of gasoline by vaporization, it is conceivable that a portion of this measured organic lead could be tetraethyllead. This could be confirmed by using a high-temperature electron-capture gas chromatography technique developed by Green (47). In the atmosphere, TEL could react with O_3 or OH radicals and ultimately be oxidized to PbO , but there is no verification of this mechanism.

Gravitational Settling, Impaction, and Rainout of Airborne Lead

All three of these processes remove lead exhaust emissions from the air and deposit them on solid and liquid surfaces. By contrast, however, gravitational settling and impaction are primarily short-range phenomena, and rainout of lead is a long-range transport and removal process. Gravitational settling is a function of the terminal settling velocity of the particle. This velocity is a function of particle size and density. Removal by impaction occurs in confined spaces such as city street canyons and highway tunnels. The long-range transport, growth, coagulation, and removal of airborne particles has been studied by Heisler et al. (48) and summarized by Seinfeld (36). Laboratory studies by Dahl and Corrin (49) have examined one mechanism for lead containing automobile exhaust emissions via precipitation—the washout process occurring below cloud base. It was concluded that rain falling through an aerosol was not a significant process of removal of airborne lead. In-cloud rainout was stated to be a more important mechanism for removal of airborne lead particles.

Creason et al. (50) set up an experimental program to determine the extent to which automobile emissions were a source of atmospheric contamination by lead and whether they remained primarily suspended or were deposited on the soil near the roadway. Dustfall and suspended particulate pollutants were collected at four sites in metropolitan Cincinnati, Ohio, for a three-month period from July-September, 1968. The collection points were located at 25 ft and 100 ft from the road, and the sites were chosen to represent various urbanization

and industrial patterns. For the three-month period, total dustfall mass flux rates ranged from 4.7 to 13.3 g/m²-month at the 25 ft locations and from 3.4 to 18.6 g/m²-month for the 100 ft locations. Dustfall mass flux rates for lead at the 25 ft sites ranged from 17 to 48 mg Pb/m²-month, and ranged from 8 to 17 mg Pb/m²-month at the 100 ft sites. The concentration of lead at the 25 ft sites for the three months averaged 3743 µg/g and averaged 2942 µg/g at the 100 ft site. Unfortunately, there was no correlation of these mass flux rates and concentrations with traffic volume. Angle et al. (51) measured dustfall rates, air concentrations, soil concentrations, boot tray concentrations (surface between top of shoe sole platform and the body of the shoe), milk, house dust, and water concentrations of lead for urban locations in Omaha, Nebraska. The air concentration of lead ranged from 0.63 to 0.29 µg Pb/m³; the dustfall rate for lead was 33 mg/m²-month in the urban area and 3 mg/m²-month in the suburbs. Soil lead concentrations ranged from 444 to 123 µg/g; boot tray lead concentrations ranged from 1000 to 283 µg/g. Lead concentrations in house dust ranged from 572 to 147 µg/g; lead concentration in milk averaged less than 0.04 µg Pb/ml; and lead concentration in water was less than 0.01 µg/g. The authors suggested that there may be a correlation with measured blood lead levels for a group of urban and suburban children, all well past the age of the pica problem, and these measured values of lead fallout rate.

Chemical Transformation of Lead Particles

Clarification of reaction mechanisms for airborne lead particles is incomplete. In earlier studies by Pierrard (52), the photodecomposition of PbBrCl was studied in chloroform. In this reaction medium, it was postulated that the mechanism of decomposition involved the release of the free halogen atoms. In earlier studies on the photodecomposition of PbCl₂ in vacuum and nonreactive ambient air by Kaldor and Somorjai (53), it was suggested that charge transfer controls the photoreaction rate which occurs via chloride ion vacancies. Chloride ion was subsequently released as atomic chlorine. In studies with actual lead exhaust emissions collected and aged in a black bag, Ter Haar et al. (19) observed that the halogen content of the lead particles dropped with a corresponding increase in concentration of lead as lead oxide and carbonate. Because of the absence of light, this suggested that halogen loss did not require photolytic initiation, and may involve decomposition by release of the halogen either as the acid, or some other unspecified mechanism.

For lead exhaust emissions which are deposited on solid surfaces by gravitational settling or impaction, the chemical transformation process of these particles is equally unclear. Samples of soil near heavily traveled streets and highways and samples of dust and dirt from curbs and parking lot areas in urban areas analyzed by Olson and Skogerboe (54) showed that the major chemical form of lead in these samples was PbSO₄. The authors reasoned that PbBrCl was converted to PbSO₄, presumably by reaction with SO₂. There was no kinetic rate information given to validate this proposed mechanism. In one of the samples, lead was present as PbO₂ and PbO.

Runoff in Water

Much of the lead particulate matter deposited on urban streets, curbs, and sidewalks will be washed away by precipitation and street cleaning operations. This run-off goes into storm sewers which empty into receiving waters. Assuming that lead in street dust is in the form of PbSO₄, the water insolubility of PbSO₄ will cause it to precipitate and become part of river, stream, and ocean sediments. The rate of removal of lead particulate emissions by this mechanism is a strong function of the amount, severity, and form of precipitation, and the frequency and efficiency of urban street cleaning operations. Whereas the weather is not predictable, urban traffic density patterns have been well established. Therefore, it is not inconceivable that lead concentrations in urban street, curb, and sidewalk dust will rise between precipitation and street cleaning episodes, and drop sharply thereafter.

Once transported to sediments, remobilization, availability and uptake by aquatic organisms and the implications of the presence of lead in water and food supplies have been the subjects of much research. There is an extensive literature on this subject, and much useful information on the geochemistry of lead is to be found in the Proceedings of the Conferences on Trace Substances in Environmental Health by the University of Missouri and held annually in Columbia since 1966. The National Academy of Sciences Report on Lead (3) also contains an extensive summary of this literature.

The chemical transformation of lead particulate emissions to PbSO₄, which settles in dust and dirt, its subsequent transport into the aquatic environment and deposition in sediments, and its uptake by aquatic organisms, is a major public health concern associated with the widespread release of trace metals such as lead to the environment. Metals may change valence and associated ligands, but the

metal itself is still present. While there are natural background levels of lead in the environment, the studies reported here concern levels of lead compounds which are substantially above background levels.

Deposition on Soils and Plants and Uptake by Plants

The deposition of lead particulate emissions on soil, the concentrations of lead as a function of distance from the highway, and the levels taken up by plants also have received extensive experimental consideration. Swaine (55) estimated the average lead content in the earth's crust to be 16 ppm, with a range of 26–200 ppm. Similarly Bowen (56) deduced an average world-wide lead content in soils of 10 ppm, with a range of 2–200 ppm. Lead particulate emissions deposited on soil can be subjected to the following transport phenomena: chemical reaction, absorption, adsorption, solubilization, leaching, runoff, microbially mediated chemical transformation, uptake by plants, re-entrainment by wind, removal by children playing in dirt, removal on shoes of people walking through the area, and other physical transport mechanisms.

Schuck and Locke (57), as a result of studies with consumer crops suggested that particulate emissions from the combustions of leaded gasolines by motor vehicles produced a surface dust coating on edible portions of the plant of which 50% could be washed off with water. Ter Haar (58) concluded from the analysis of plants grown at different distances from highways that the main source of lead in crops was derived from the natural pool already available to the plant in the soil. With regard to direct absorption of particulate lead emissions through the leaf surface (foliar uptake), a number of other studies (59–61) do not reach any definitive conclusions. The suggestion that particulate lead emission were simply deposited as a washable layer on plants, was the general opinion of these authors. Arvik and Zimdahl (62) found that very small quantities of lead deposited on foliage as PbBrCl were able to pass the cuticular membrane and the epicuticular waxes and actually become a part of the plant structure.

Unpublished results for soils treated with radio-labeled $^{210}\text{Pb}(\text{NO}_3)_2$ (63) have shown that this soluble form of lead is not readily taken up by either barley or soybeans. Simultaneously, an analysis of the effect on soil microbial populations was undertaken for soils treated with 1, 10, and 100 μg Pb/g dry weight of soil. These studies were designed to examine the mechanisms of microbially mediated processes that make metals more available for

transport across root membranes and translocation within the plant. The natural lead concentration of the soil before treatment was 5 $\mu\text{g/g}$. Therefore, these additions represented substantial increases in the total quantities of lead in the soil.

The soil used in this study was a Ritzville (Andic Aridic Haplustoll) soil. The soil pH was 7.6 and the cation-exchange capacity was 5.8 mg/100 g. Based on an oven dry basis, the organic matter totaled 1.2 wt-%, total nitrogen was 0.068 wt-%, sand (particles $> 50 \mu\text{m}$) was 23.3 wt-%, silt (particles between 2 and 50 μm) was 63.1%, and clay (particles $< 2 \mu\text{m}$) was 12.6 wt-%. For the three increments of soluble lead salt additions to this soil type, there were no observed effects on microbial numbers or respiratory activity. In addition, there was very little reduction in crop yields as a function of increasing lead addition to the soil. It was concluded that for these two particular varieties of plants, a mechanism operating at the soil-root interface excluded from uptake all but a very small amount of lead. Part of the mechanism of exclusion may have been that the microbial populations do not metabolically transform lead into a form which is more easily transported across the soil-root interface. If so, this may explain the low phytotoxicity of lead to these two plant varieties. A recent literature review on lead in soils and plants has been prepared by Zimdahl and Arvik (64).

Two species of grasses (*Agrostis tenuis* and *Agrostis stolonifera*) and a variety of wild oats (*Avena fatua*) can tolerate high soil concentrations of lead, and show substantial growth on land that would be considered contaminated. Populations of these two grasses which are tolerant to high levels of zinc, copper, lead, and nickel in soil have been described by Bradshaw (65), Jowett (66, 67), and Gregory and Bradshaw (68). Rains (69) has studied the growth and accumulation of lead by wild oats (*Avena fatua*) growing on contaminated land near a lead smelter. In a related study, Smith (70) has presented data on the accumulation of lead and mercury by urban trees.

Beyond the recognition that lead particulate emissions deposited on solid surfaces can be re-entrained during high winds or by turbulent wakes induced by vehicular traffic, there is not much information on this removal mechanism. It can be postulated that vehicular traffic can grind larger size particles to smaller size material which can be re-entrained either by traffic turbulence or windy meteorological conditions. At present, there are no data on breakage functions for particulate lead emissions. Even though the contribution to airborne lead from this mechanism is not known precisely, Sehmel and Lloyd (71) have shown that par-

ticles can be transported over great distances by successive deposition and resuspension. Measurements of lead deposition fluxes and airborne lead concentrations at various heights above large open surfaces have supported this hypothesis. Such lead profiles were measured over a building roof in Pasadena, California, by Davidson et al. (72).

Observations by Lepow et al. (73) of the "mouthing" behavior of ten children who had been playing in an area where the average soil lead concentration was found to be 11,000 $\mu\text{g/g}$, and the average lead concentration of dirt on the hands was 2400 $\mu\text{g/g}$, have suggested that this may be a significant mechanism of absorption by children. Similarly, Vostal et al. (74) observed that the ingestion of house dust containing large concentrations of lead from the hands may be a source of a substantial intake of lead in children.

Rate of Accumulation of Particulate Lead Emissions

The final term in the mass balance describes the rate of accumulation of lead particles in a geographic region after the rate of removal has been subtracted from the rate of entry. Since lead particles can be partitioned between air, water, and solid phases, this term must consider not only the accumulation of lead in each of these phases, but also the rate of exchange between phases. Therefore, the time scale for this term is an important factor.

Airborne lead concentration gradients and soil lead content gradients have been determined at varying distances from roadways in urban and rural areas by many authors. Average airborne lead concentrations have been measured for both urban and rural areas. These concentrations and concentration gradients are point values which have been determined over a specific time, and may or may not represent the time-dependent characteristics of lead concentrations for a particular geographic area. Even so, the questions of greatest concern are where and at what rate does lead accumulate. Therefore, these point values are important indicators and provide a strong incentive to provide a unified method to explain these observed situations.

Daines et al. (75) present data on atmospheric lead levels as a function of traffic volume and distance from the roadway. Dedolph et al. (59) have determined soil concentrations for lead as a function of distance from a roadway carrying an average vehicle load of 29,000 vehicle/day. They derive an expression for mapping soil lead concentrations at different location sites from the roadway. Kinard et al. (76) have measured lead concentration patterns

in soil for an urban setting in Columbia, South Carolina. A city block with variable vehicle loads on the streets in this area was used in this study. Hemphill et al. (77) determined lead concentration gradients in soil at right angles to a roadway in Missouri used to haul lead ore to a smelter. Ter Haar and Aronow (78) presented concentration profiles for lead in soil at varying distances between a road and a house painted with a high lead content paint, and between a road and a brick house. As the house painted with lead-based paint was approached, the soil concentration dropped then rose to approximately twice the concentration of lead measured at or near the roadway. For the brick house, the soil lead concentration measured at or near the roadway declined until a position half way between the road and the street was reached. The concentration then increased at the brick house was approached but did not reach the average concentration measured near the road. The implication was that the flaking of lead-based paint was a major contributor of lead to soil near buildings painted with high-content lead paints. Recently, Solomon and Hartford (79) have offered contradictory evidence concerning lead sources in and around buildings in a small urban community. In and around well-kept homes painted with low lead paints, lead levels in dust and dirt within the homes averaged 600 ppm and 680 $\mu\text{g/m}^2$ and outside the residence; dust had lead concentrations between 600–1950 ppm and 90–6640 $\mu\text{g/m}^2$. In this community the main source was attributed to automotive traffic.

It has been stated earlier that the problems associated with solving the time-dependent atmospheric dispersion equations have resulted in approximate methods of solution. A method which attempts to overcome these difficulties and simulate macroscopic trends and effects for short-range transport and accumulation of lead in the vicinity of a highway is the box or compartment model proposed by Watkins (80) and Vaitkus et al. (81). The model treats each phase of the environment as a compartment. The contents of each compartment are assumed to be well-mixed. Transfers between phases are described by transfer coefficients. The formulated model is a set of linear, first-order, ordinary differential equations with variable coefficients which are determined from experimental data. Input consists of initial conditions, physical system characteristics, meteorological parameters, and source characteristics. The output gives the amounts of lead in each compartment or sector of the environment as a function of time and space. When applied to a divided highway, approximately 56% of the lead consumed during combustion was deposited on the soil within 100m of the highway by

gravitational settling (82): 22% was removed by long-range airborne transport and approximately 22% of the lead consumed remained in the vehicle. Less than 0.5% of the lead deposited on soil was transported below the top layers of soil. By using this scheme, validated models can be constructed to predict temporal and spacial changes in lead concentration in different compartments of an urban region. In this manner, the extent of exposure to lead in an urban area can be followed.

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